Preparation and properties of $ZnBr(CF_3) \cdot 2L$ – a convenient route for the preparation of CF_3I

Dieter Naumann*, Wieland Tyrra, Birgit Kock
Institut für Anorganische Chemie, Universität Köln, Greinstr. 6, D-50939 Köln (Germany)

Werner Rudolph and Bernd Wilkes
Solvay Fluor und Derivate, Hans-Böckler-Allee 20, D-30173 Hannover (Germany)

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Abstract

$ZnBr(CF_3) \cdot 2L$ ($L = DMF$, CH_3CN) can easily be prepared by the reactions of $CBrF_3$ with elemental zinc in better than 60% yield. The reaction of $ZnBr(CF_3) \cdot 2DMF$ with iodine monochloride in DMF solution yields pure CF_3I in better than 70% yield via an ecologically less damaging reaction pathway than the decarboxylation route using silver or mercury trifluoroacetates.

Introduction

$Zn(CF_3)$ derivatives have been prepared by several methods. They have been obtained either by alkyl–trifluoromethyl group exchange reactions [1, 2] or by the electrochemically-initiated oxidative addition of CF_3I to elemental zinc in the presence of α,α'-bipyridine [3]. A further similar synthetic route is the reaction of $CBrF_3$ with elemental zinc in pyridine or DMF suspensions which lead to poorly reactive compounds, $ZnBr(CF_3) \cdot 2L$ and $Zn(CF_3)_2 \cdot 2L$ [4]. In addition, reactions of difluorodihalogenomethanes [5] or trifluoromethyl radicals [6] with elemental zinc afford the formation of $Zn(CF_3)$ derivatives.

Trifluoroiodomethane, CF_3I, can be prepared either by the reaction of CI_4 with IF_5 [7] or by the thermal decarboxylation of silver [8] or mercury [9] trifluoroacetates in the presence of elemental iodine. Reactions of $Hg(CF_3)_2$, $Hg(CF_3)I$ [10], $Zn(CF_3)$ complexes [5] and $Cd(CF_3)$ complexes [5, 11] with elemental iodine or $Bi(CF_3)_3$ [12] and $Cd(CF_3)_2$ complexes [11] with iodine monochloride also yield CF_3I; however, most of these compounds can only be prepared selectively using CF_3I as a reactant.

Herein, we report a facile preparative laboratory route for the synthesis of $ZnBr(CF_3)$ complexes from $CBrF_3$ and elemental zinc and a new synthetic pathway for CF_3I from the starting materials $ZnBr(CF_3) \cdot 2DMF$ and ICl.

Experimental

Elemental zinc was purchased from Riedel-de Haën, Seelze (Germany); iodine monochloride from Schuchardt, Hohenbrunn (Germany). $CBrF_3$ was received from Solvay Fluor und Derivate, Hannover as a gift. All solvents were used as received without any further purification.

The ^{19}F NMR spectra were recorded on a Bruker model AC 200 spectrometer (^{19}F, 188.3 MHz) and the ^{13}C NMR spectra on a Bruker model AM 300 spectrometer (^{13}C, 75.4 MHz) with positive shifts being downfield from the external standard CCl_3F (^{19}F) and the internal standard TMS (^{13}C).

Preparation of $ZnBr(CF_3) \cdot 2DMF$

Zinc dust (20 g, 0.30 mmol) was suspended in 200 ml DMF at ambient temperature in a 500 ml round-bottom flask equipped with one screw closure and two gas distribution tubes with straight-way cocks (Fig. 1). Elemental iodine (1 g) was added to the suspension. $CBrF_3$ was bubbled into the suspension until the pressure reached a value of *c.* 3500 hPa. The reaction mixture became yellow to green in colour with the evolution of heat; the pressure decreased. After *c.* 30 min, the $CBrF_3$ pressure was again increased to 4000 hPa. The straight-way cock was closed and the reaction mixture stirred overnight at room temperature. The resulting yellow to brown solution was filtered to remove unreacted elemental zinc. The solvent (DMF) was distilled off under reduced pressure. A pale brown solid remained

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*Author to whom correspondence should be addressed.

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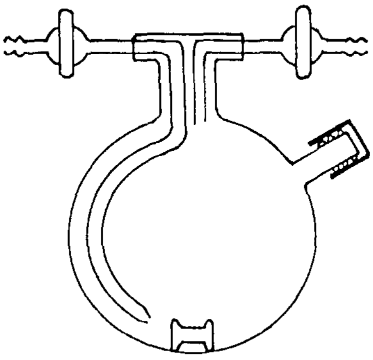

Fig. 1. Arrangement employed for the preparation of complexes.

which was dried *in vacuo* (1×10^{-3} hPa). The crude $ZnBr(CF_3)\cdot 2DMF$ could be washed with CCl_3F or toluene to obtain the product as a white to yellow crystalline solid with a decomposition point of 99–100 °C. The yield was *c.* 60%. ^{19}F NMR (CD_3CN): $\delta(CF_3)$ -42.6 (s) ppm, $^{1}J(^{19}F-^{13}C)=358.3$ Hz, $^{1}\Delta(^{19}F-^{12/13}C)$ 0.1388 ppm. $^{13}C\{^{1}H\}$ NMR (CD_3CN): $\delta(CF_3)$ 145.5 (q) ppm, $^{1}J(^{19}F-^{13}C)=358.3$ Hz; $\delta(C{=}O)$ 165.8 ppm; $\delta(CH_3)$ 37.6 and 32.3 ppm.

Preparation of $ZnBr(CF_3)\cdot 2CH_3CN$

The procedure was similar to that for $ZnBr(CF_3)\cdot 2DMF$. The reaction temperature was held at 30 °C with the pressure not exceeding 2000 hPa. A higher pressure caused a decrease in yield. The crude product could be used as obtained or be purified by the method described for the DMF complex. The yield was *c.* 75%. ^{19}F NMR (CD_2Cl_2): $\delta(CF_3)$ -47.9 (s) ppm, $^{1}J(^{19}F-^{13}C)=355.1\pm0.7$ Hz, $^{1}\Delta(^{12/13}C-^{19}F)$ 0.1400 ppm.

Preparation of CF_3I

Using the reaction apparatus shown in Fig. 2, 200 g of $ZnBr(CF_3)\cdot DMF$ solution containing *c.* 15.1% by weight bromide (*c.* 13% by weight trifluoromethyl groups) was introduced at ambient temperature. Then 60 g ICl dissolved in 30 ml DMF was poured slowly into the solution. The CF_3I formed during the exothermic reaction was distilled off continuously and condensed into two cold traps maintained at Dry Ice temperature. The yield of CF_3I was better than 90% relative to ICl; the product did not contain impurities such as CHF_3.

Elemental iodine could also be used in place of ICl.

Results and discussion

$ZnBr(CF_3)$ complexes were formed from zinc dust and $CBrF_3$ in many solvents such as DMF, acetonitrile, pyridine, THF and polyethers with donor properties. The most suitable donor solvents for obtaining stable

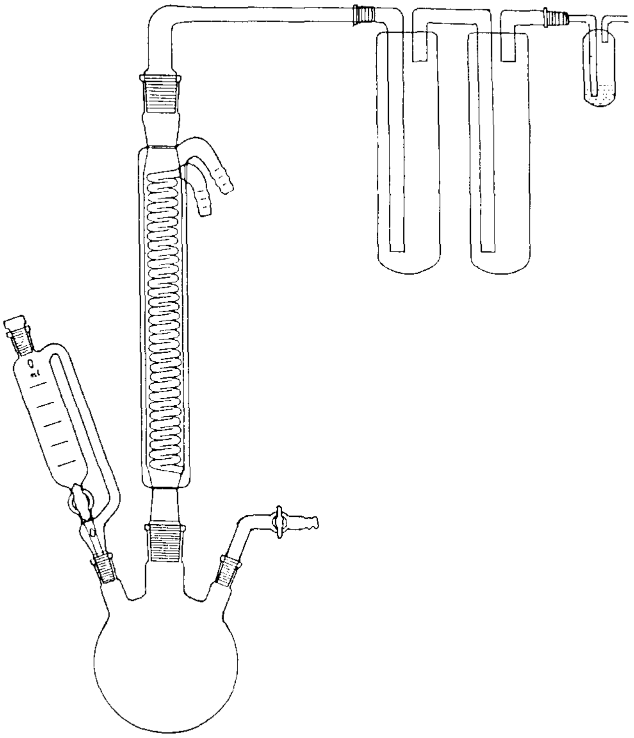

Fig. 2. Reaction apparatus used for the preparation of CF_3I.

$ZnBr(CF_3)$ complexes without the formation of large amounts of by-products are DMF and acetonitrile. The reactions probably proceed via a SET mechanism [13] which is commenced either by elemental iodine or by ultrasonic or electrochemical irradiation [14]. The complexes isolated with DMF or CH_3CN are 1:2 adducts.

$$Zn + CBrF_3 \xrightarrow{L} ZnBr(CF_3)\cdot 2L$$

The complex $ZnBr(CF_3)\cdot 2L$ undergoes Schlenk-type equilibria as described for Grignard reagents [15] and pentafluorophenylzinc halides [16].

$$2ZnBr(CF_3)\cdot 2L \rightleftharpoons Zn(CF_3)_2\cdot 2L + ZnBr_2\cdot 2L$$

Hence, in the ^{19}F NMR spectra of these compounds, the signal for $Zn(CF_3)_2\cdot 2L$ can be detected *c.* 2 ppm downfield from the resonance for $ZnBr(CF_3)\cdot 2L$ [4]. The intensity of the $Zn(CF_3)_2\cdot 2L$ signal depends on the concentration of the solution as well as on the storage time of the original solution. The longer a solution is stored, the greater the extent to which the equilibrium is shifted to the right-hand side of the above equation. However, this change in the position of the equilibrium has no influence on the reactivity of the system.

The addition of iodine monochloride to the reaction mixture allows the preparation of CF_3I via a polar reaction pathway [17].

$$ZnBr(CF_3)\cdot 2L + I^{+} + Cl^{-} \longrightarrow ZnBrCl\cdot 2L + CF_3I$$

This route provides a suitable means for obtaining CF_3I in an ecologically less damaging way than the decarboxylation route using silver or mercury trifluoroacetates [8, 9]. Additionally, the possibility of using ICl instead of elemental iodine, as is usual in common procedures for obtaining CF_3I, avoids the formation of metal iodides and lowers the effective costs.

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